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Mechanisms of Fire Suppression by Superagents

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To date the most commonly used and effective fire extinguishing agents are Halon 1301 (CF₃Br) and Halon 1211 (CF₂ClBr), which are halogenated compounds that are known to be strong destroyers of stratospheric ozone and are consequently no longer produced. Thus, most of the current flame inhibition research is focused on finding alternatives to the halon agents. Besides halogen based inhibitors, there exist several other agents, such as iron pentacarbonyl, (Fe(CO)₅), that inhibit flames even more effectively than Halon and are thus classified as superagents. Unfortunately Fe(CO)₅ cannot be used in occupied spaces because it is highly toxic¹, but identifying its chemical suppression mechanism will help direct the future development of replacement agents that are as effective, but not as deleterious.

When an inhibiting agent is introduced into a non-premixed flame through either the fuel or air streams, chemical inhibition arises from the lowering of the concentration of radicals through scavenging reactions. It is well known that CF_3Br homogeneously suppresses and/or extinguishes a flame by scavenging H atoms which affects the concentration of OH· via the reaction $H_2O + H \Leftrightarrow OH + H_2$. Flame suppression by metal-containing agents, such as $Fe(CO)_5$, is often assumed to proceed by a similar pathway as $CF_3Br^{2,3}$ but additional paths such as metal-containing particulate forming and undergoing heterogeneous free-radical recombination on the surface can contribute as well¹.

The flames investigated here are supported on an opposed flow burner which is operated at 50 torr. The base flame consists of methane delivered from the bottom duct and synthetic air (nitrogen plus oxygen) delivered from the upper duct. The visible flame lies between the two ducts on the air side of the flow field stagnation plane. Both agents CF₃Br, Fe(CO)₅ are separately delivered to the flame front via the oxidizer duct.

Assuming that the primary suppression mechanism for $Fe(CO)_5$ is via scavenging H atoms, we have mapped OH· concentrations using laser induced fluorescence throughout doped and undoped flames as a surrogate monitor of the H atom behavior. Numerical calculations based on homogeneous chemistries predict temperatures and OH· concentrations to be relatively unaffected until near-extinction limits are reached which has been demonstrated in preliminary experiments in CF_3Br doped flames. However, experimental measurements of temperatures and OH· concentrations in $Fe(CO)_5$ doped flames, reveal monotonic decreases with addition of $Fe(CO)_5$. These results suggest that additional suppression paths could be occurring for $Fe(CO)_5$.

^{1.} Pitts, W.M., Nyden, M.R., Gann, R.G., Mallard, W. G., and Tsang, W., in *Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives*, NIST Technical Note 1279, US Department of Commerce, Chapter 3: Section J., pp. 73-74.

2. Reinelt, D., and Linteris, G.T., *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1996, 1421-1428.

^{3.} Reinelt, D., Linteris, G.T., and Babushok, V., Chemical and Physical Processes in Combustion, 1996, 273-276.